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Influence of the Temperature-Ramp on Mass Transfer Effects during Temperature-Programmed Desorption from Porous Catalysts

The influence of mass transfer effects on temperature-programmed desorption (TPD) spectra from porous catalysts has been examined from the standpoints of nondimensional analysis (*1*) and numerical simulation of specific models (*2, 3*). Considerable attention has been focused on the interaction of H_2 and CO over Group VIII metal supported catalysts (*2, 3*). It has been proposed that with proper design of experimental conditions, mass transfer effects will result in a negligible error in interpreting kinetic parameters from TPD spectra of individual adsorbates (*3*). On the other hand, it has been shown that readsorption effects cannot be eliminated for any reasonable combination of experimental conditions (*2, 4*). In the absence of mass transfer limitations and under conditions of equilibrium adsorption, reasonably accurate estimates of the enthalpy of adsorption can be obtained using a theoretical relationship, which is independent of the transport model used to describe flow through the porous bed of catalyst (*3, 4*).

Gorte (*1*) has proposed that intraparticle concentration gradients can be minimized by reducing catalyst particle size and carrier gas flow rate. This criterion was obtained by nondimensionalization of the differential equations governing mass transfer during TPD (*2*) and appears to provide a suitable basis for predicting the onset of intraparticle mass transfer effects (*3*). This work assumes that this condition is met and considers the applicability of a convenient procedure that has been proposed (*3*) for mathematically simulating thermal desorption from porous adsorbent particles. This method is an alternative to the dispersion model and introduces the concept of a mixing cell (*5, 6*). In such a model, the number of mixing cells in a cascade of mixing cells is chosen such that axial dispersion of gas-phase species is accurately described: as axial dispersion becomes more significant, the number of mixing cells that simulate this dispersion decreases.

For a fixed bed of catalyst particles operating under *isothermal* conditions, the equivalent length of a perfect mixing cell (no axial dispersion) is given by (*5, 6*)

$$\Delta z = \frac{2\,\mathrm{De}}{\bar{u}}, \tag{1}$$

where $\bar{u}$ is the interstitial fluid velocity, and De is the effective dispersion coefficient. This latter quantity can be expressed in terms of a molecular diffusivity via a tortuosity factor and a bed porosity (*5*). From the definition of Δz, the number N of mixing cells required to describe mass transfer effects in the axial direction can be defined (*6*) as

$$N = \frac{L_b}{\Delta z}, \tag{2}$$

where L_b is the bed length.

Rieck and Bell (*3*) showed that N can be related to the properties of the catalyst particles by

$$N = \frac{m}{R_b^2 D_p \rho_p (1 - \varepsilon_b)} \left(\frac{D_p}{\Delta z}\right), \tag{3}$$

where R_b is the radius of the bed, D_p is the particle diameter, ρ_p is the catalyst density, m is the mass of catalyst, and ε_b is the bed

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porosity. Butt (*5*) has presented an empirical correlation of the form

$$\frac{\Delta z}{D_p} = \frac{0.6}{\text{ScRe}} + \frac{1}{(1 + 3.8/\text{ScRe})} \tag{4}$$

which is approximately valid for $0.01 < \text{ScRe} < 500$ (*5*). While this analytical representation is not exact, an examination of the original data compiled by Wen and Fan (*7*) does demonstrate the accuracy of the correlation over this range of ScRe.

In Eq. (4) the product of the Schmidt number and Reynolds number is given by

$$\text{ScRe} = \frac{\bar{u}D_p}{\text{Dm}}, \tag{5}$$

where Re is the particle Reynolds number and Dm is the molecular diffusivity. The latter quantity can be obtained from the numerous correlations (*8–11*) given in standard texts.

It is of interest to examine the consequence of employing the mixing-cell model to describe mass transport during the *nonisothermal* operation of a TPD experiment. This communication points out that if the number of mixing cells required to describe axial dispersion at the starting temperature of a TPD experiment is greater than 1, then the required number of cells will decrease with increasing temperature. Combining Eqs. (2), (4), and (5) shows explicitly that N is proportional to $T^{-1/2}$. To quantify these observations and for the purpose of demonstration we consider the desorption of CO into a carrier gas of helium. Table 1 lists typical parameter values that have been used (*3*). Temperature-dependent values are reported at 298 K. Table 2 shows the effect of increasing temperature—the procedure used to accomplish a TPD experiment—on the quantities of interest for use in Eq. (4) to predict N from Eq. (5). The number of mixing cells decreases with increasing temperature and thus Δz increases.

TABLE I

Parameter Values Used to Calculate ScRe

D_p	0.04 cm
m	108 mg
ε_p	0.4
ε_p	0.7
ρ_p	0.63 g/cm^3
d_p	10^{-6} cm
Q	2 cm^3/sec (298 K)
R_b	0.5 cm
Dm (*8*)	0.684 cm^2/sec (298 K)
Dm (*9*)	0.709 cm^2/sec (298 K)
Dm (*10*)	0.794 cm^2/sec (298 K)
Dm (*11*)	0.488 cm^2/sec (298 K)

TABLE 2

Effect of Increasing Temperature on Dm, ScRe, N, and Δz

Quantity[a] Temperature (K):	298	400	500	600	700	800
Re (gas)	2.07	1.71	1.48	1.32	1.19	1.09
Re (particle)	0.21	0.17	0.15	0.13	0.12	0.11
Gorte criterion[b]	0.20	0.23	0.26	0.28	0.31	0.33
Dm_1 (*8*)	0.684	1.146	1.691	2.327	3.048	3.850
Dm_2 (*9*)	0.709	1.149	1.659	2.255	2.928	3.645
Dm_3 (*10*)	0.794	1.358	2.039	2.843	3.766	4.804
Dm_4 (*11*)	0.488	0.758	1.060	1.393	1.755	2.144
ScRe_1	0.372	0.298	0.253	0.220	0.196	0.177
ScRe_2	0.359	0.297	0.258	0.227	0.204	0.188
ScRe_3	0.321	0.252	0.210	0.180	0.159	0.142
ScRe_4	0.522	0.451	0.403	0.368	0.341	0.319
N_1	5.34	4.36	3.73	3.27	2.93	2.66
N_2	5.18	4.35	3.80	3.37	3.04	2.80
N_3	4.67	3.72	3.12	2.70	2.38	2.14
N_4	7.16	6.33	5.74	5.29	4.94	4.64
Δz_1	0.068	0.083	0.097	0.111	0.124	0.137
Δz_2	0.070	0.084	0.096	0.108	0.120	0.130
Δz_3	0.078	0.098	0.117	0.135	0.153	0.170
Δz_4	0.051	0.057	0.063	0.069	0.074	0.078

[a] Subscripts refer to values of molecular diffusivity calculated from indicated references.

[b] Gorte criterion <1 (*3*) for absence of intraparticle diffusion.

If N is found to be greater than one at the onset of a TPD experiment and constrained to be a constant, the axial concentration gradient will be overestimated. Correspondingly, in the temperature range from 298 to 800 K during a TPD experiment, Eq. (1) must be obeyed if the mixing-cell model is to remain valid. Preserving this equality introduces a contradiction to accepted concepts because it would require the tortuosity, which is a constant (*12*), to change with temperature. For example, for the parameters used and taking Dm from the equation of Fuller (*8*), the tortuosity would vary from 3 to 1.7 over this temperature range. It is interesting to note that for N to be unity over the temperature range considered and assuming $\varepsilon_b = 0.4$ and the tortuosity to be 4 (*12*), the molecular diffusivity would have to be 5.21 cm^2/sec at 298 K and 14 cm^2/sec at 800 K.

Proper design of the experimental conditions, such that $N = 1$ at the maximum temperature at which desorption is to be measured, is a viable means of utilizing the simplicity of the mixing-cell model. Although, bed geometries can be designed, in general, the transport properties of the adsorbate cannot be controlled by the experimentalist. Thus we conclude from this analysis that in the absence of intraparticle diffusion the proper description of mass transfer effects on TPD from a bed of catalyst perfused by a flow of carrier gas requires a nonsteady mass balance which includes both axial dispersion and convective transport (*13*).

APPENDIX: NOMENCLATURE

De	effective diffusivity, Dm $\varepsilon_b/\tau + \bar{u}D_p/2$, cm^2/sec
Dm	molecular diffusivity, cm^2/sec
D_p	particle diameter, cm
d_p	pore diameter, cm
L_b	length of catalyst bed, cm
m	catalyst mass, g
N	number of CSTR's used to represent the catalyst bed
Pe	Peclet number, $\bar{u}D_p$/De
Q	volumetric flow rate, cm^3/sec
R_b	bed radius, cm
Re	Reynolds number, $\rho_g\bar{u}D_p/\mu_g$
R_p	particle radius, cm
Sc	Schmidt number, μ_g/ρ_gDm
$\bar{u}$	interstitial velocity, u/ε_b, cm/sec
u	superficial velocity based on tube diameter, cm/sec
Δz	equivalent length of a perfect mixing cell, cm
ε_b	catalyst bed void fraction
ε_p	catalyst particle void fraction
μ_g	gas viscosity, g cm/sec
ρ_g	gas density, g/cm^3
ρ_p	catalyst particle density, g/cm^3
τ	tortuosity

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